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Crowned and liquid-crystalline phthalocyanines as gas-sensor materials

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Abstract

Semiconducting films of crown-ether substituted metal-free phthalocyanines are shown to have unique properties of fast response and reversal to NO_2 at room temperature. Increasing the size of the crown ring or complexing the phthalocyanine with Cu(II) gives slower responses. Complexing the crown-ether rings with simple metal salts leads to very rapid reversible conductivity *decreases* in 1–5 ppm NO_2 at room temperature. Discotic liquid-crystal phases of octaoctyl phthalocyanine also respond rapidly and reversibly to NO_2. The origins of these effects are discussed with reference to reduced local polarizability, increased molecular separation and improved molecular assembly, and experiments exploring the influence of molecular design and crystal engineering on these sensing properties are described.

1. Introduction

Although the sensitivity of semiconducting gas sensors based on sublimed films of conventional metal phthalocyanine complexes is excellent, offering detection of NO_2 down to ppb levels, for example, their response rate and reversibility are generally lower than the optimum for a practical sensing device. The latter properties appear to be influenced by both the chemical and physical structure of the films [1], and although there are numerous reports in the literature of attempts to optimize these structures, very little success has been achieved in producing materials that respond and reverse rapidly at room temperature. However, recently two new classes of substituted phthalocyanines have been synthesized, which offer new prospects for optimizing both the chemical and physical properties of the films via controlled modification of the strength of gas adsorption and by the use of molecular self-assembly to provide improved structural order in the films. In the first of these, four crown-ether rings are attached to the periphery of the phthalocyanine molecule [2] (Fig. 1), while in the second class alkyl or alkoxy substituents are attached to either the α- or β-positions of the outer six-membered rings of the phthalocyanine molecule [3–5]. In both of these two classes of compounds, the substituents have lower polarizability than the π-electron system of the phthalocyanine nucleus, and can also act as spacer groups between adjacent phthalocyanine molecules [6]. These two properties provide a means of controlling the strength of the surface charge-transfer interaction, which is fundamental to the sensing mechanism, by varying the size of the crown rings or the lengths of the alkyl or alkoxy groups. Furthermore, complex formation between the crown-ether groups and a range of metal salts promotes molecular assembly by introducing ionic interactions into the molecular crystalline film. Thus, cations which fit into the crown cavity attract counter-anions to intercalate between adjacent rings, while cations too large for the cavity act as bridges of two adjacent molecules, with ordered molecular stacking promoted in both cases. Many of the alkyl- or alkoxy-substituted phthalocyanines exhibit thermotropic transitions to discotic liquid-crystalline phases, with shorter spacings between adjacent phthalocyanine cores as the alkyl groups become more mobile [7], which also improves molecular assembly

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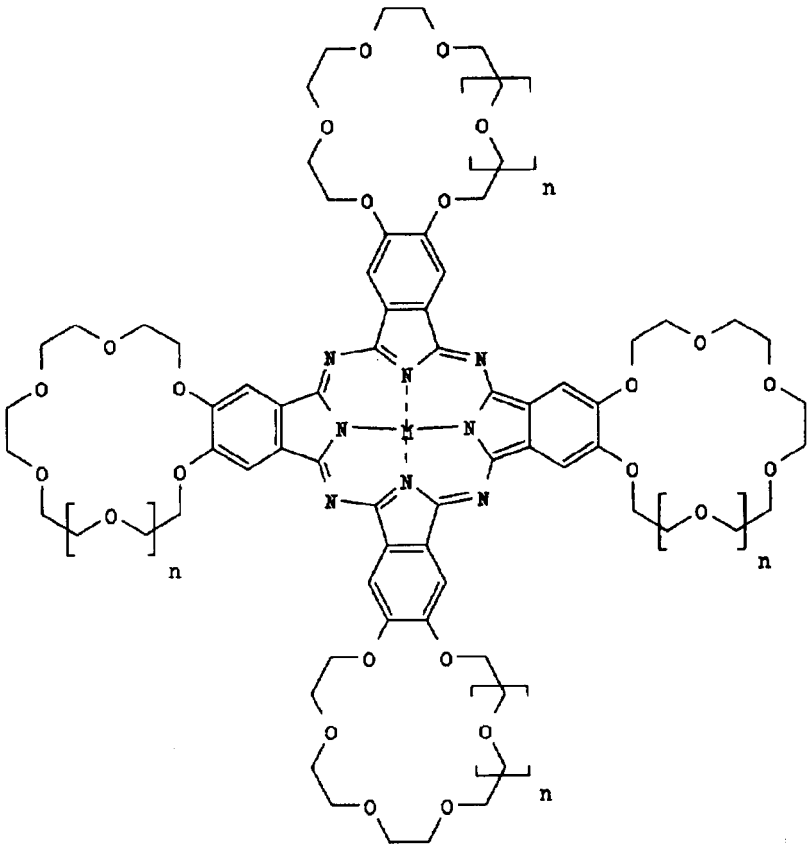

Fig. 1. Crown-ether substituted phthalocyanines (M=2H or Cu; $n=0$, 1 or 2).

into ordered stacks. In this paper we report studies of the NO_2-sensing properties of films of these materials.

2. NO_2 sensing by crown-ether substituted phthalocyanines

2.1. Response characteristics before complexing the crown ethers

Films deposited from chloroform solution on alumina substrates show responses to 1–5 ppm NO_2 which are much faster and more reversible than for any other phthalocyanine films previously studied at room temperature. Figure 2 shows data for the 15-crown-5 metal-free derivative exposed to 1, 2, 3, 4 and 5 ppm NO_2 in dry air for 2 min, with reversal in clean air for 2 min between each exposure. The response to 1 ppm NO_2 nearly reaches equilibrium within 2 min and the reversal is also nearly complete within the same time. The fast kinetics result from the weakening of the surface charge-transfer interactions resulting from the lower polarizability of the immediate surroundings of each adsorption site. The energy needed to transfer an electron from the phthalocyanine film to an adsorbed electron-acceptor gas is determined by the ionization potential of the phthalocyanine, the electron affinity of the gas and the polarization energies of the resulting

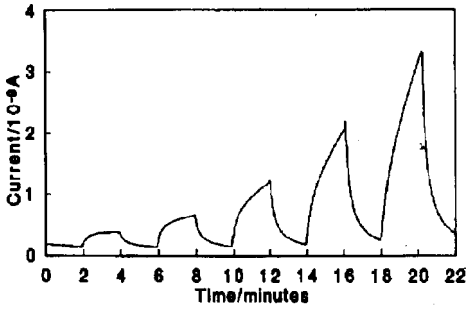

Fig. 2. The semiconductivity changes for a film of 15-crown-5 metal-free phthalocyanine at room temperature exposed to clean dry air for 2 min then to 1, 2, 3, 4 and 5 ppm NO_2 in dry air for 2 min periods with reversal in clean dry air for 2 min after each exposure.

charged species. Reducing the local polarizability reduces the polarization energies and weakens surface charge-transfer interactions. The calibration curve for 1–5 ppm NO_2 is shown in Fig. 3. Similar experiments with the 18-crown-6 and 21-crown-7 derivatives [8] show that the response and reversal become slower as the crown ring is made larger. This is due to the increased lateral separation of adjacent molecules, reducing lateral repulsions between adsorbed species which are believed to promote fast kinetics of adsorption and desorption [9]. Similar experiments with the corresponding copper

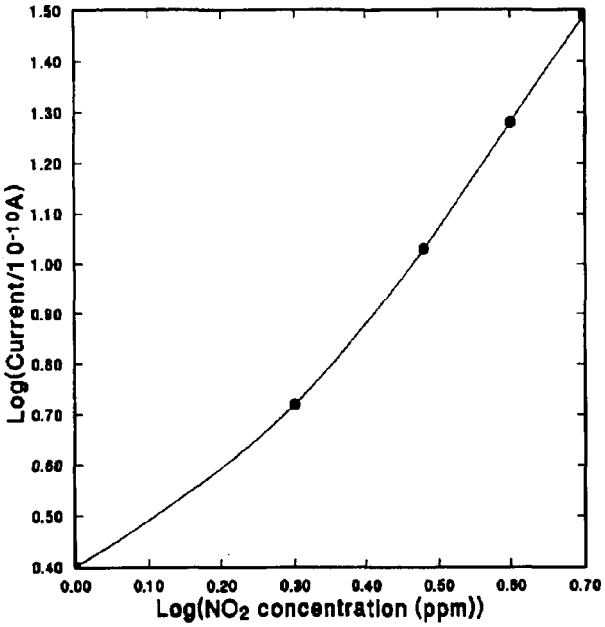

Fig. 3. Calibration curve for 15-crown-5 metal-free phthalocyanine in 1–5 ppm NO_2.

phthalocyanine complexes [8] show slower response and reversal. This is due to the well-known tendency of Cu(II) to prefer tetragonal six-fold coordination in a Jahn–Teller distorted environment, resulting in stronger adsorption of electron-acceptor gases and weaker lateral repulsions between adsorbed species (which are most isolated from each other when near the centre of the phthalocyanine molecule).

2.2. *Response characteristics after complexing with metal salts*

Treatment of the above films with one drop of an aqueous solution containing 1 g dm^{-3} KCl led to their dissolution and reconstruction. Scanning electron microscope photographs before and after treatment showed a dramatic improvement in surface smoothness, which appears to be a consequence of the improved molecular assembly discussed in the Introduction. This is also reflected in the semiconductivity changes, which are totally different from those of the untreated films. Figure 4 shows the response of the KCl-treated 21-crown-7 metal-free phthalocyanine to the same sequence of NO_2 exposures as in Fig. 2, also at room temperature. Similar results were obtained for the other materials, and the *decrease* in conductivity on exposure to the electron-accepting gas suggests that the film initially has n-type conductivity in clean air, in contrast to the p-type behaviour of most normal phthalocyanine films. This unexpected result suggests that the tighter structure excludes oxygen from the bulk of the KCl-treated film, the conductivity now being determined by residual donor impurities. The overall conductivity of the film remains

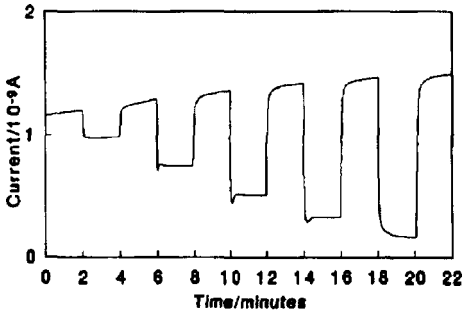

Fig. 4. Room-temperature response of a KCl-treated 21-crown-7 metal-free phthalocyanine film exposed to 1–5 ppm NO_2 as for Fig. 2.

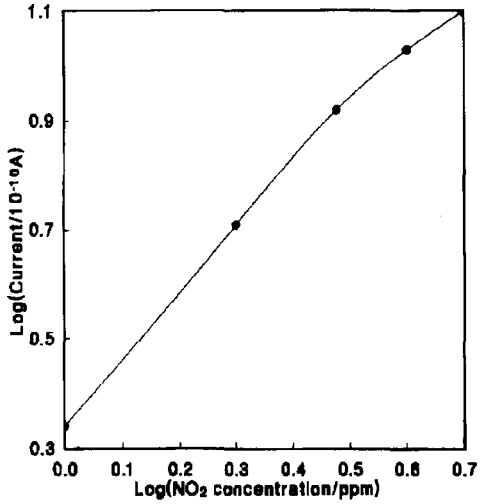

Fig. 5. Calibration curve for KCl-treated 21-crown-7 metal-free phthalocyanine in 1–5 ppm NO_2.

comparable to that of the untreated material, the improved ordering leading to higher carrier mobility compensating for lower carrier density. The extremely rapid response and reversal arise from the uniformity of the surface structure, which minimizes the strong adsorption sites, grain boundaries and pathways for slow diffusion of gases into the bulk of the film, which are all contributors to slow components in the response. Further experiments show that at high NO_2 concentrations the magnitude of this n-type response decreases as depletion is more complete, and eventually the response becomes a more normal p-type. This depletion is already obvious in a downturn of the calibration curve (Fig. 5) towards higher concentrations. The process of film dissolution and reconstruction is difficult to achieve reproducibly, so further experiments have been carried out using films cast from solutions of the crowned phthalocyanine and a salt soluble in a common solvent (e.g., KSCN in DMF). These films have very uniform surfaces and give rapid conductivity *increases* on exposure to NO_2 at room temperature, suggesting that the larger anion allows oxygen into the film while

still effectively promoting the molecular assembly that favours the very fast response and reversal.

2.3. *Experiments with related molecules*

Films of an analog of the 15-crown-5 phthalocyanine in which the outermost oxygen in each crown ring is replaced by N-acetyl [10] show a fast reversible response to NO_2 at room temperature, which is not changed by treatment with KCl. This is as expected from the above discussion, since the low polarizability of the crown rings is still effective in giving weaker adsorption and hence faster response, while the acetyl group effectively blocks the crown cavity, preventing complexation with KCl. However, when a fully tosylated 2,5,9,12-tetra-azacyclopentadecine-substituted phthalocyanine was used (similar to the nitrogen analog of the tetra 12-crown-4 phthalocyanine), the film was a very poor semiconductor which gave no apparent change on exposure to gas or on treatment with KCl. The bulky tosyl groups effectively prevent overlap of the π-electron clouds of adjacent phthalocyanine molecules, drastically reducing carrier mobility. These experiments provide improved understanding of the scope for molecular design for improved performance, as well as increasing confidence in the proposed interpretations.

3. NO_2 sensing by discotic liquid crystalline phthalocyanines

Films of 1,4,8,11,15,18,22,25-octa-octyl phthalocyanine were deposited from chloroform solution and subjected to the same cycle of NO_2 exposures as described above, at various temperatures. This material transforms from a crystalline to a liquid-crystalline phase on heating to 84.5 °C, attaining a fan-textured D_1 discotic phase at 101 °C in which columnar stacks of cofacial molecules are arranged in a hexagonal packing with the columns perpendicular to the substrate plane [7]. A dramatic improvement in NO_2-sensing properties was observed at 110 °C, with fast response to equilibrium conductivity, and complete reversal in clean air, within 2 min (Fig. 6(b)). At room temperature such responses showed no sign of equilibration and only partially reversed (Fig. 6(a)). This result suggests that similar film uniformity to that reported above for the KCl-doped crowned phthalocyanines can also be achieved in the discotic phase, with a superior calibration curve showing no curvature due to depletion effects (Fig. 7). Further studies should reveal similar size-trends to those seen for the crowned phthalocyanines as the alkyl group chain length is varied. To obtain the most uniform discotic phase, the material should ideally be cooled slowly from the melt, but in practice this was not possible since the molten material contracted into a

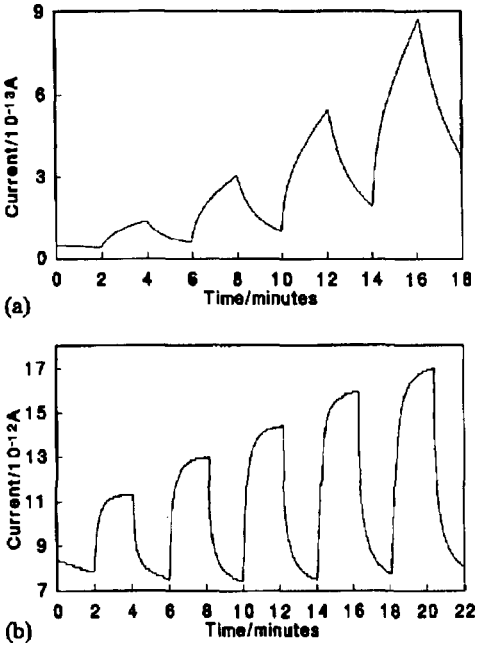

Fig. 6. Response of a film of 1,4,8,11,15,18,22,25-octaoctyl phthalocyanine exposed to NO_2 as for Fig 2: (a) 1–4 ppm at room temperature; (b) 1–5 ppm at 110 °C.

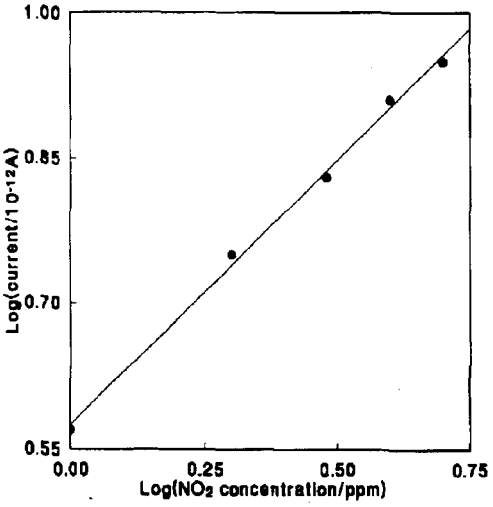

Fig. 7. Calibration curve for octaoctyl phthalocyanine at 110 °C in 1–5 ppm NO_2.

globule on a wide range of substrate materials. Preliminary studies suggest that this problem may be overcome by using a related material with seven decyl groups and one hydrophilic–C_3H_6OH group.

4. Conclusions

Both these approaches to molecular design to control the strengths of surface interactions and improve molecular assembly yield materials with substantially superior sensor performance to that of conventional or Langmuir–Blodgett phthalocyanine films. The liquid-

crystal approach is at a slight disadvantage because of the comparative difficulty in preparing well-purified materials, as well as the need to operate the films at elevated temperatures. There is considerable scope for further development of the crown-ether approach, both synthetically and via different complexing procedures. This work has significantly enhanced our understanding of the factors influencing the response of phthalocyanine materials as gas sensors, and greatly improves the prospects for developing effective simple yet sensitive semiconductor sensors for electron-accepting gases.

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